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Lithium secondary battery, useful in portable telephone set, contains phosphoric compound, and material absorbing or storing lithium metal or lithium alloy forming positive electrode active material

Patent Assignee: NIPPON TELEGRAPH & TELEPHONE CORP (NITE)

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Patent Details:

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Abstract (Basic): JP 2001085010 A

NOVELTY - This lithium secondary battery contains a phosphoric acid compound having olivine structure. An element X is a material being electrochemically stable in a 3 - 4V potential region, based on the standard potential of a lithium metal, in a state to constitute the phosphoric acid compound. Further, this battery contains a material absorbing and discharging a lithium metal, a lithium alloy, or lithium ion, as a positive electrode active material. Further, lithium ion contains a material, effecting movement to effect electric chemical reaction to the positive electrode active material and the negative electrode active material, as electrolyte.

DETAILED DESCRIPTION - The phosphoric acid compound has formula $\text{Li}_{1-y}\text{X}_y\text{PO}_4$ where $0 < y < 1$ is satisfied. y is less than or equals 0.3.

USE - Useful in a portable telephone set and a note type personal computer.

ADVANTAGE - Economical efficiency is improved and battery characteristics are excellent.

pp; 8 DwgNo 0/6

Title Terms: LITHIUM; SECONDARY; BATTERY; USEFUL; PORTABLE; TELEPHONE; SET;
CONTAIN; PHOSPHORIC; COMPOUND; MATERIAL; ABSORB; STORAGE; LITHIUM; METAL;
LITHIUM; ALLOY; FORMING; POSITIVE; ELECTRODE; ACTIVE; MATERIAL

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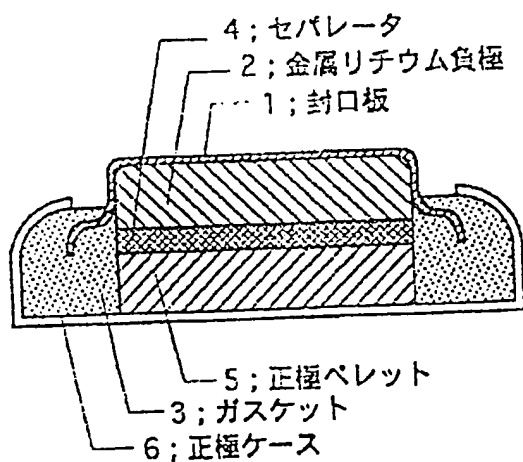
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(54) [Title of the Invention] **Lithium Secondary Cell**

(57) [Summary]

[Object] To improve discharge capacity at a practically acceptable current level in a lithium secondary cell in which the positive electrode is obtained using an inexpensive iron lithium phosphate material that can be charged and discharged at a voltage of 4 V or less. A positive electrode active material 5 is obtained using a material that is a phosphate compound whose olivine structure is expressed by the general formula $[\text{Li}]_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$), that remains electrochemically stable in the potential range of 3 V to 4 V in relation to the standard potential of lithium metal when element X is a component of the phosphate compound, and that has an y-value of $0 < y \leq 0.3$.

[Merits] Discharge capacity or cycle characteristics are improved during charging and discharging at 4 V or less, which is a potential at which cell life is less likely to be adversely affected by the decomposition of a liquid electrolyte when compared with the use of an unsubstituted iron lithium phosphate.



[Key to figure: 1: sealing plate, 2: negative electrode (lithium metal), 3: gasket, 4: separator, 5: positive electrode pellet, 6: positive electrode casing]

[Claims]

[Claim 1] A lithium secondary cell, characterized by comprising a positive electrode active material in the form of a material that is a phosphate compound whose olivine structure is expressed by the general formula $\text{Li}_2\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$), that remains electrochemically stable in the potential range of 3 V to 4 V in relation to the standard potential of lithium metal when element X is a component of the phosphate compound, and that has an y-value of $0 < y \leq 0.3$; a negative electrode active material in the form of a material capable of occluding and releasing lithium metal, lithium alloys, or lithium ions; and an electrolytic substance in the form of a substance capable of allowing lithium ions to migrate in order to be able to react electrochemically with the positive or negative electrode active material.

[Claim 2] A lithium secondary cell as defined in Claim 1, characterized in that the element X in the phosphate compound is at least one element selected from magnesium, cobalt, nickel, and zinc.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a lithium secondary cell, and more particularly to an improved positive electrode active material. The present invention seeks to provide a cell with enhanced discharge capacity and improved charge/discharge cycle characteristics.

[0002]

[Prior Art] Lithium secondary cells whose negative electrode active materials are capable of occluding and releasing lithium metal, lithium alloys, or lithium ions are characterized by high voltage and excellent reversibility. In particular, lithium ion secondary cells in which complex oxides of lithium and transition metals are used as positive electrode active materials, and carbonaceous materials as negative electrode active materials, are lighter and have better capacity than conventional lead secondary cells, nickel-cadmium secondary cells, or the like, and are therefore widely used in portable phones, notebook computers, and other electronic devices.

[0003] In current practice, LiCoO_2 is primarily employed as the positive electrode active material for the commonly used lithium ion secondary cells, but cobalt, which is the starting material for LiCoO_2 , is scarce and can be extracted only at a limited number of locations, thus making this starting material unsuitable as the positive electrode active material of lithium ion secondary cells both in terms of cost and in terms of stable supply.

[0004] By contrast, LiFePO_4 , which is obtained using inexpensive and plentiful iron as a starting material, can function as the positive electrode active material of a lithium secondary cell, as disclosed in JP (Kokai) 9-134725 and the like. It is also disclosed in JP (Kokai) 9-134724 that cell voltage can be controlled by substituting cobalt for the iron in LiFePO_4 .

[0005]

[Problems Which the Invention Is Intended to Solve] A drawback, however, is that using LiFePO_4 slows down reactions in which lithium is introduced and desorbed during cell charging and discharging, while using coarser LiFePO_4 particles in order to increase the density with which the positive electrode active material is packed into the cell allows full-capacity charging and discharging to be carried out only at extremely low electric currents.

[0006] Another feature is that adding cobalt to LiFePO_4 allows cobalt redox reactions to occur at a high potential (about 5 V with respect to the standard potential of lithium metal), but when the charging voltage exceeds 4.3 V, oxidative degradation begins to affect the liquid electrolytes of the lithium ion secondary cells currently in use, making it much more likely that cycle characteristics will be adversely affected when the cells are charged or discharged at such a high voltage. Liquid electrolytes that remain stable at high voltage levels are being developed, but practical solutions have yet to be found, and adding cobalt in excessive amounts is still unacceptable both in terms of cost and in terms of cell life.

[0007] Consequently, an object of the present invention, which was perfected in order to overcome the above-described shortcomings of the prior art, is to improve the discharge capacity at a practically acceptable current level in a lithium secondary cell in which the

positive electrode is obtained using an inexpensive iron lithium phosphate material that can be charged and discharged at a voltage of 4 V or less.

[0008]

[Means Used to Solve the Above-Mentioned Problems] Aimed at attaining the stated object, the lithium secondary cell pertaining to the present invention is characterized by comprising a positive electrode active material in the form of a material that is a phosphate compound whose olivine structure is expressed by the general formula $\text{Li}_2\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$), that remains electrochemically stable in the potential range of 3 V to 4 V in relation to the standard potential of lithium metal when element X is a component of the phosphate compound, and that has an y-value of $0 < y \leq 0.3$; a negative electrode active material in the form of a material capable of occluding and releasing lithium metal, lithium alloys, or lithium ions; and an electrolytic substance in the form of a substance capable of allowing lithium ions to migrate in order to be able to react electrochemically with the positive or negative electrode active material.

[0009] The lithium secondary cell pertaining to the present invention is also characterized in that the element X in the phosphate compound in accordance with the present invention is at least one element selected from magnesium, cobalt, nickel, and zinc.

[0010] The present invention will now be described in further detail. The positive electrode active material of the lithium secondary cell in accordance with the present invention is a material that is a phosphate compound whose olivine structure is expressed by the general formula $\text{Li}_2\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$), that remains electrochemically stable in the potential range of 3 V to 4 V in relation to the standard potential of lithium metal when element X is a component of the phosphate compound, and that has an y-value of $0 < y \leq 0.3$.

[0011] A substance commonly referred to as iron lithium phosphate is expressed as LiFePO_4 ($z = 1$) and is such that further lithium introduction is impossible to achieve without altering the structure. Using this material as the positive electrode of a cell allows lithium to be constantly removed from the positive electrode and causes the composition to

approach that of FePO_4 (that is, the value of z to decrease) during charging. When the charged cell is discharged, the lithium in the liquid electrolyte is introduced into the positive electrode, and the composition returns to that of LiFePO_4 ($z = 1$). A material that satisfies the condition $z = 1$ is considered to be the best choice when cell manufacture and discharge capacity are taken into account, but because the value of z varies continuously, using a material that has a disproportionate composition (for example, one with $z = 0.9$) still makes it possible to fabricate a cell that operates by a mechanism similar to that provided by a common proportionate iron lithium phosphate satisfying the condition $z = 1$. This is the reason that the value of z in the above formula must satisfy the condition $0 < z \leq 1$.

[0012] In a lithium secondary cell in which LiFePO_4 is used for the positive electrode active material, charging is accompanied by the desorption of lithium and the conversion of iron ions from a divalent state to a trivalent state. Lithium desorption causes the crystal structure (olivine structure) to become unstable in the desorbed areas and leads to partial blockage of lithium migration routes, which, coupled with the impaired desorption of lithium from inner areas, is believed to prevent lithium secondary cells in which LiFePO_4 is used for the positive electrode active material from developing adequate capacity at an acceptable charge/discharge current.

[0013] It is also believed that such structural instability causes discharge capacity to be reduced by repeated charge/discharge cycles. By contrast, partially replacing the iron with zinc and other elements that remain electrochemically stable in the potential range of 3 V to 4 V in relation to the standard potential of lithium metal in a phosphate compound allows the zinc and other replacement elements to remain bivalent and to resist oxidation during charging, and permits lithium, which is adjacent to the replaced elements, to remain in the crystal without being desorbed. For this reason, it is believed that the replaced regions are less likely to change their crystal structure and are capable of retaining their lithium migration routes during charging, resulting in higher capacity and enhanced cycle stability.

[0014] However, undesorbed lithium does not contribute to charging or discharging, so excessive replacement may result in reduced cell capacity. As a result of extensive experimentation, the inventors discovered that the iron element replacement considered effective for achieving enhanced capacity should be 30% ($0 < y \leq 0.3$) or less, preferably 10–30% ($0.1 \leq y \leq 0.3$), and ideally 10–20% ($0.1 \leq y \leq 0.2$).

[0015] As used herein, the term "element that remains electrochemically stable in the potential range of 3 V to 4 V in relation to the standard potential of lithium metal" refers to an element that undergoes oxidation and reduction at a potential less than 3 V in relation to the standard potential of lithium metal and remains stable at higher voltages (as is the case with alkali metals, alkaline-earth metals, and the like), or to an element that reduces to metal from a bivalent state at a potential less than 3 V in relation to the standard potential of lithium metal, resists oxidation or reduction in the potential range of 3 V to 4 V, and oxidizes from a bivalent state to a trivalent state at a potential greater than 4 V when substituted for the iron in iron lithium phosphate (as is the case with cobalt, nickel, or the like).

[0016] Consequently, the substituent metals are not limited to transition metals and may also include traditional metals. Ions that are bivalent in the potential range of 3 V to 4 V should be used in order to replace the iron while preserving the olivine structure of iron lithium phosphate. Magnesium, cobalt, nickel, zinc, and the like are particularly preferred as such substituent elements.

[0017]

[Working Examples] Working examples of the present invention will now be described in further detail with reference to the accompanying drawings. The present invention is not limited by these working examples, however.

[0018]

[Working Example 1] Fig. 1 is a cross-sectional cell view depicting a structure fashioned in accordance with a working example of the lithium secondary cell pertaining to the present invention. In the drawing, 1 is a scaling plate, 2 a negative electrode (lithium

metal), 3 a gasket, 4 a separator, 5 a positive electrode pellet, and 6 a positive electrode casing.

[0019] The positive electrode active material ($\text{LiFe}_{0.7}\text{Co}_{0.3}\text{PO}_4$) contained in the positive electrode pellet 5 (Fig. 1) was produced in the following manner.

[0020] Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 0.5:0.7:0.3:1, and were then baked for 24 hours at 800°C in an argon atmosphere. Fig. 2 shows an X-ray diffraction chart of the resulting material.

[0021] The chart is virtually identical to the X-ray diffraction chart (JCPDS 15-0760) reported for LiFePO_4 , suggesting that the iron is replaced while the olivine structure remains unchanged. The positive electrode active material (70 wt%) was kneaded together with acetylene black (conductive agent; 25 wt%) and polytetrafluoroethylene (binder; 5 wt%) into a clayey mass, which was rolled with two rolls to a thickness of about 0.6 mm and then stamped out with a punch into a diskoid shape with a diameter of 15 mm, yielding a positive electrode pellet 5. Fig. 3 shows the olivine structure of LiFePO_4 . The black circles indicate lithium atoms; the octahedrons, iron surrounded by six oxygens; and the tetrahedrons, phosphorus surrounded by four oxygens.

[0022] An assembly (obtained by a method in which a negative electrode 2 composed of lithium metal was pressed against a sealing plate 1 made of stainless steel) was subsequently inserted into a recess formed by a polypropylene gasket 3, a porous separator 4 (polypropylene) and the positive electrode pellet 5 were placed on the negative electrode in the order indicated, a liquid electrolyte obtained by dissolving LiPF_6 in an isovolumetric mixed solvent of ethylene carbonate and dimethyl carbonate to a concentration of 1 mol/dm^3 was added in an appropriate amount as an electrolyte to impregnate the assembly, and the components were sealed in a positive electrode casing 6 (stainless steel), yielding a coin-shaped cell with a thickness of 2 mm and a diameter of 23 mm. The charge/discharge characteristics of the resulting cell were evaluated at a

constant current of 1 mA under conditions corresponding to a terminal charge voltage of 4.0 V and a terminal discharge voltage of 3.0 V.

[0023] Fig. 4 depicts a charge/discharge curve obtained after ten cycles. It can be seen that the discharge potential is substantially the same as the voltage of a cell whose positive electrode is obtained using a known unsubstituted iron lithium phosphate and whose negative electrode is obtained using lithium metal, and that the cell is charged and discharged by the oxidation and reduction of iron ions. The discharge capacity increases somewhat between the first and tenth cycles, and remains substantially constant thereafter.

[0024] The capacity of the 50th cycle was 5.6 mAh. Fig. 5 shows the relation between the number of cycles and the discharge capacity during the initial 50 cycles. Fig. 6 shows the relation between the extent y to which iron was substituted by element X and the discharge capacity of the 50th cycle. Table 1 shows the compositional formula of the positive electrode active material used in the cell, the amount of substitution y , and the discharge capacity of the 50th cycle.

[0025]

[Comparative Example 1] A positive electrode active material (LiFePO_4) devoid of element X was prepared in the following manner. Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 0.5:1:1, and were then baked for 24 hours at 800°C in an argon atmosphere.

[0026] A positive electrode pellet and a coin-shaped cell were then fabricated in the same manner as in Working Example 1 by making use of the positive electrode active material thus obtained. Charge/discharge characteristics were evaluated under the same conditions as in Working Example 1, and although the discharge capacity of the first cycle was higher than that demonstrated by the cell obtained in Working Example 1, the discharge capacity of the fifth and later cycles was less than that of the cell obtained in Working Example 1, and was only 4.7 mAh (which constituted 84% of the cell capacity achieved in Working Example 1) during the 50th cycle.

[0027] Fig. 5 shows the relation between the number of cycles and the discharge capacity during the initial 50 cycles. Fig. 6 shows the relation between the extent y to which iron was substituted by element X and the discharge capacity of the 50th cycle. Table 1 shows the compositional formula of the positive electrode active material used in the cell, the amount of substitution y , and the discharge capacity of the 50th cycle. Data for Working Example 1 are also presented.

[0028]

[Table 1] Compositional Formulas of Positive Electrode Active Materials, Amounts of Substitution y , and Discharge Capacities During 50th Cycle in Cells of Working and Comparative Examples

Working and comparative examples	Compositional formula	Amount of substitution y	Discharge capacity during 50 th cycle (mAh)
Working Example 1	$\text{LiFe}_{0.7}\text{Co}_{0.3}\text{PO}_4$	0.3	5.6
Working Example 2	$\text{LiFe}_{0.8}\text{Co}_{0.2}\text{PO}_4$	0.2	6.7
Working Example 3	$\text{LiFe}_{0.9}\text{Co}_{0.1}\text{PO}_4$	0.1	4.9
Working Example 4	$\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$	0.2	7.0
Working Example 5	$\text{LiFe}_{0.85}\text{Mg}_{0.15}\text{PO}_4$	0.15	6.8
Working Example 6	$\text{LiFe}_{0.8}\text{Ni}_{0.2}\text{PO}_4$	0.2	6.5
Comparative Example 1	LiFePO_4	0	4.7
Comparative Example 2	$\text{LiFe}_{0.6}\text{Co}_{0.4}\text{PO}_4$	0.4	4.3

[0029]

[Working Example 2] A positive electrode active material ($\text{LiFe}_{0.8}\text{Co}_{0.2}\text{PO}_4$) contained in a positive electrode pellet was produced in the following manner. Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 0.5:0.8:0.2:1, and were then baked for 24 hours at 800°C in an argon atmosphere.

[0030] A positive electrode pellet and a coin-shaped cell were then fabricated in the same manner as in Working Example 1 by making use of the positive electrode active material thus obtained. Charge/discharge characteristics were evaluated under the same conditions as in Working Example 1, and it was found that the discharge capacity of the second and subsequent cycles was greater than that of the cell obtained in Comparative Example 1, and that during the 50th cycle the capacity was 6.7 mAh, or 1.43 times that of the cell obtained in Comparative Example 1.

[0031] Fig. 5 shows the relation between the number of cycles and the discharge capacity during the initial 50 cycles. Fig. 6 shows the relation between the extent y to which iron was substituted by element X and the discharge capacity of the 50th cycle. Table 1 shows the compositional formula of the positive electrode active material used in the cell, the amount of substitution y , and the discharge capacity of the 50th cycle. The characteristics obtained in Working Example 1 and Comparative Example 1 are also presented.

[0032]

[Working Example 3] A positive electrode active material ($\text{LiFe}_{0.9}\text{Co}_{0.1}\text{PO}_4$) contained in a positive electrode pellet was produced in the following manner. Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 0.5:0.9:0.1:1, and were then baked for 24 hours at 800°C in an argon atmosphere.

[0033] A coin-shaped cell was then fabricated in the same manner as in Working Example 1 by making use of the positive electrode active material thus obtained. Charge/discharge characteristics were evaluated under the same conditions as in Working Example 1, and it was found that the discharge capacity of the fifth and subsequent cycles was greater than that of the cell obtained in Comparative Example 1, and that during the 50th cycle the capacity was 4.9 mAh, or 1.04 times that of the cell obtained in Comparative Example 1.

[0034] Fig. 5 shows the relation between the number of cycles and the discharge capacity during the initial 50 cycles. Fig. 6 shows the relation between the extent y to which iron was substituted by element X and the discharge capacity of the 50th cycle. Table 1 shows the compositional formula of the positive electrode active material used in the cell, the amount of substitution y , and the discharge capacity of the 50th cycle. The characteristics obtained in Working Examples 1 and 2 and in Comparative Example 1 are also presented.

[0035]

[Comparative Example 2] A positive electrode active material ($\text{LiFe}_{0.6}\text{Co}_{0.4}\text{PO}_4$) contained in a positive electrode pellet was produced in the following manner. Lithium carbonate (Li_2CO_3), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 0.5:0.6:0.4:1, and were then baked for 24 hours at 800°C in an argon atmosphere.

[0036] A coin-shaped cell was then fabricated in the same manner as in Working Example 1 by making use of the positive electrode active material thus obtained. Charge/discharge characteristics were evaluated under the same conditions as in Working Example 1, and it was found that the discharge capacity between the first and 50th cycles was always lower in comparison with the cell obtained in Comparative Example 1, and that during the 50th cycle the capacity was merely 4.3 mAh, or 0.91 times that of the cell obtained in Comparative Example 1.

[0037] Fig. 5 shows the relation between the number of cycles and the discharge capacity during the initial 50 cycles. Fig. 6 shows the relation between the extent y to which iron was substituted by element X and the discharge capacity of the 50th cycle. Table 1 shows the compositional formula of the positive electrode active material used in the cell, the amount of substitution y , and the discharge capacity of the 50th cycle. The characteristics obtained in Working Examples 1–3 and Comparative Example 1 are also presented.

[0038]

[Working Example 4] A positive electrode active material ($\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$) contained in a positive electrode pellet was produced in the following manner. Lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 0.5:0.8:0.2:1, and were then baked for 24 hours at 800°C in an argon atmosphere.

[0039] A coin-shaped cell was then fabricated in the same manner as in Working Example 1 by making use of the positive electrode active material thus obtained. Charge/discharge characteristics were evaluated under the same conditions as in Working Example 1, and it was found that the discharge capacity of the first and subsequent cycles was greater than that of the cell obtained in Comparative Example 1, and that the dependence on the number of cycles was somewhat more pronounced than in Working Example 2. During the 50th cycle, the capacity was 7.0 mAh, or 1.49 times that of the cell obtained in Comparative Example 1.

[0040] Fig. 5 shows the relation between the number of cycles and the discharge capacity during the initial 50 cycles. Table 1 shows the compositional formula of the positive electrode active material used in the cell, the amount of substitution y , and the discharge capacity of the 50th cycle. The characteristics obtained in Working Examples 1–3 and Comparative Examples 1 and 2 are also presented.

[0041]

[Working Example 5] A positive electrode active material ($\text{LiFe}_{0.85}\text{Mg}_{0.15}\text{PO}_4$) contained in a positive electrode pellet was produced in the following manner. Lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$), iron oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), magnesium oxide (MgO), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 1:0.85:0.15:1, and were then baked for 24 hours at 800°C in an argon atmosphere.

[0042] A coin-shaped cell was then fabricated in the same manner as in Working Example 1 by making use of the positive electrode active material thus obtained.

Charge/discharge characteristics were evaluated under the same conditions as in Working Example 1, and it was found that the discharge capacity of the first and subsequent cycles was greater than that of the cell obtained in Comparative Example 1, and that the dependence on the number of cycles was substantially the same as in Working Example 2.

[0043] During the 50th cycle, the capacity was 6.8 mAh, or 1.45 times that of the cell obtained in Comparative Example 1. Table 1 shows the compositional formula of the positive electrode active material used in the cell of Working Example 5, the amount of substitution y , and the discharge capacity of the 50th cycle. The characteristics obtained in Working Examples 1–4 and Comparative Examples 1 and 2 are also presented.

[0044]

[Working Example 6] A positive electrode active material ($\text{LiFe}_{0.8}\text{Ni}_{0.2}\text{PO}_4$) contained in a positive electrode pellet was produced in the following manner. Lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$), iron acetate ($(\text{CH}_3\text{COO})_2\text{Fe}$), nickel oxide (NiO), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) were first mixed and introduced as starting materials into a crucible in a molar ratio of 1:0.8:0.2:1, and were then baked for 24 hours at 800°C in an argon atmosphere.

[0045] A coin-shaped cell was then fabricated in the same manner as in Working Example 1 by making use of the positive electrode active material thus obtained. Charge/discharge characteristics were evaluated under the same conditions as in Working Example 1, and it was found that the discharge capacity of the first and subsequent cycles was greater than that of the cell obtained in Comparative Example 1, and that the dependence on the number of cycles was somewhat less than in Working Example 2. During the 50th cycle, the capacity was 6.5 mAh, or 1.38 times that of the cell obtained in Comparative Example 1. Table 1 shows the compositional formula of the positive electrode active material used in the cell of Working Example 6, the amount of substitution y , and the discharge capacity of the 50th cycle. The characteristics obtained in Working Examples 1–5 and Comparative Examples 1 and 2 are also presented.

[0046] Although the above working examples were described with reference to cases in which a material fashioned into a pellet was used for the positive electrode, it is also possible to use a product (such as a coated electrode) obtained by a method in which a positive electrode active material and a binder such as polyvinylidene fluoride are added to a solvent such as *N*-methyl-2-pyrrolidone, a slurry is prepared, this slurry is thinly applied to a metal foil, and the coated foil is dried.

[0047] Although lithium metal was used as the negative electrode active material, it is also possible to use lithium metal, a carbonaceous material (graphite, coke, or the like), a metal oxide (tungsten oxide, niobium oxide, vanadium oxide, tin oxide, or the like), a lithium/transition metal complex nitride (lithium manganese nitride, lithium cobalt nitride, lithium iron nitride, or the like), a metal chalcogenide (iron sulfide, molybdenum sulfide, or the like), or the like.

[0048] Although the liquid electrolyte used was obtained by dissolving LiPF_6 in an isovolumetric mixed solvent of ethylene carbonate and dimethyl carbonate to a concentration of 1 mol/dm^3 , it is also possible to use the same materials as those employed for conventional nonaqueous lithium secondary cells.

[0049] Examples of such solvents include dimethoxyethane, 2-methyltetrahydrofuran, ethylene carbonate, methyl formate, dimethyl sulfoxide, propylene carbonate, acetonitrile, dimethyl carbonate, diethyl carbonate, and methyl ethyl carbonate, which may be used either singly or as mixtures of two or more components.

[0050] LiClO_4 , LiBF_4 , LiAsF_6 , LiCF_3SO_3 , and the like may also be used as solutes in addition to the LiPF_6 used in the working examples. Polymer electrolytes, solid electrolytes, salts that melt at normal temperature, and the like can also be used. Various conventional materials can also be used as elements of separators, cell casings, and other structural materials. In addition, the working examples were described with reference to cells shaped as buttons, but cylindrical, angular, and other shapes may also be used without any particular restrictions.

[0051]

[Merits of the Invention] As described above, the lithium secondary cell pertaining to the present invention is such that discharge capacity or cycle characteristics can be improved during charging and discharging at 4 V or less (which is a potential at which it is less likely that cell life will be adversely affected by the decomposition of a liquid electrolyte when compared with the use of an unsubstituted iron lithium phosphate) by the use of a positive electrode active material in the form of a compound obtained by a method in which the iron of the iron lithium phosphate is substituted in a ratio of 30% or less with a material that remains electrochemically stable in the potential range of 3 V to 4 V in relation to the standard potential of lithium metal, with iron still a component of the phosphate compound.

[Brief Description of the Figures]

[Figure 1] A cross-sectional view depicting a structure fashioned in accordance with a working example of the lithium secondary cell pertaining to the present invention.

[Figure 2] A diagram depicting an X-ray diffraction pattern of the $\text{LiFe}_{0.7}\text{Co}_{0.3}\text{PO}_4$ used as a positive electrode active material in Working Example 1 of the inventive lithium secondary cell.

[Figure 3] A diagram depicting the olivine structure of LiFePO_4 .

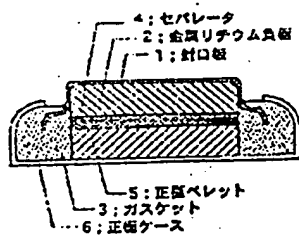
[Figure 4] A diagram depicting the discharge capacity curve of the cell pertaining to Working Example 1 of the inventive lithium secondary cell.

[Figure 5] A diagram depicting the relation between the number of cycles and the discharge capacity in Working Examples 1–4 of the inventive lithium secondary cell, together with the same relation for Comparative Examples 1 and 2.

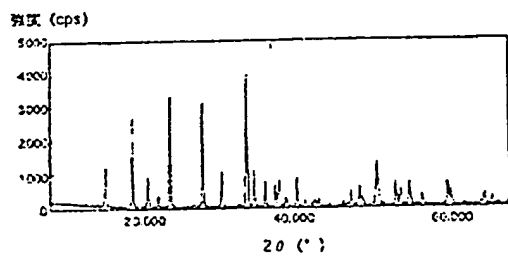
[Figure 6] A diagram depicting the relation between discharge capacity and the extent y to which iron was substituted by element X in Working Examples 1–3 of the inventive lithium secondary cell, together with the same relation for Comparative Examples 1 and 2.

[Key]

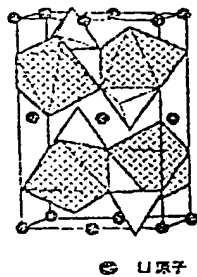
1: sealing plate, 2: negative electrode (lithium metal), 3: gasket, 4: separator,
5: positive electrode pellet, 6: positive electrode casing



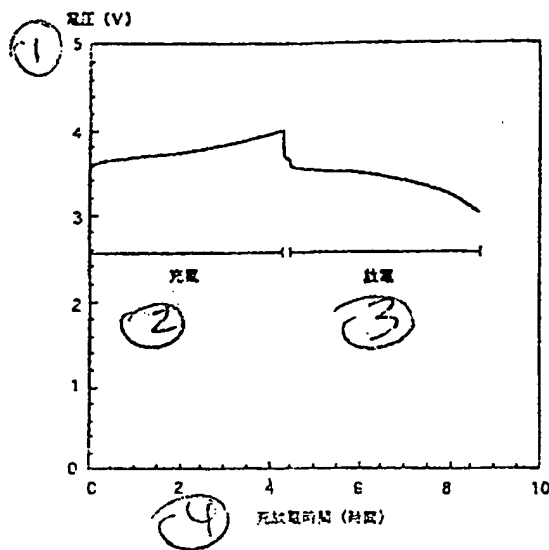
[Key to figure 1: 1: sealing plate, 2: negative electrode (lithium metal), 3: gasket, 4: separator, 5: positive electrode pellet, 6: positive electrode casing]



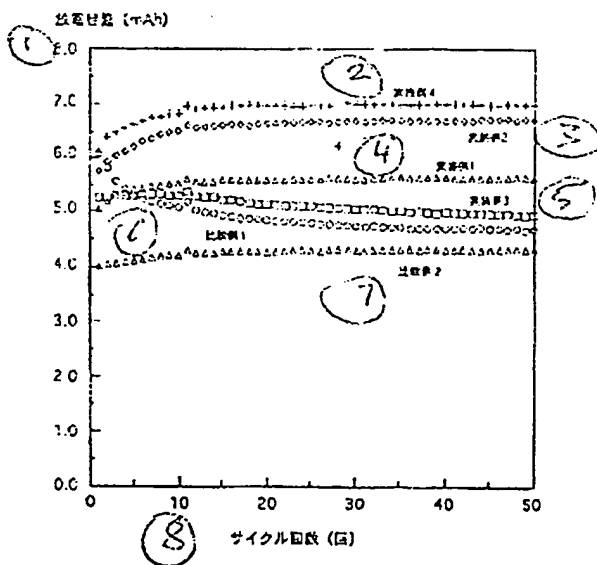
[Key to figure 2: Intensity (cps)]



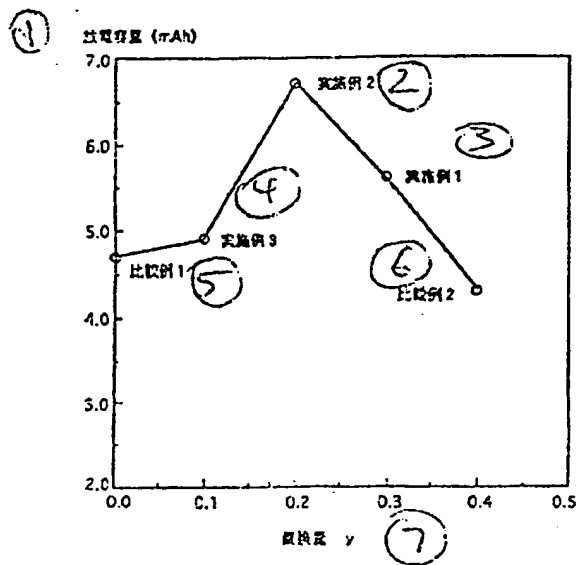
[Key to figure 3: Li atom]



[Key to figure 4: 1: voltage (V), 2: charge, 3: discharge, 4: charge/discharge time (hours)]



[Key to figure 5: 1: discharge capacity (mAh), 2: Working Example 4, 3: Working Example 2, 4: Working Example 1, 5: Working Example 3, 6: Comparative Example 1, 7: Comparative Example 2, 8: number of cycles (times)]



[Key to figure 6: 1: discharge capacity (mAh), 2: Working Example 2, 3: Working Example 1, 4: Working Example 3, 5: Comparative Example 1, 6: Comparative Example 2, 7: amount of substitution y]

(Continued from front page)

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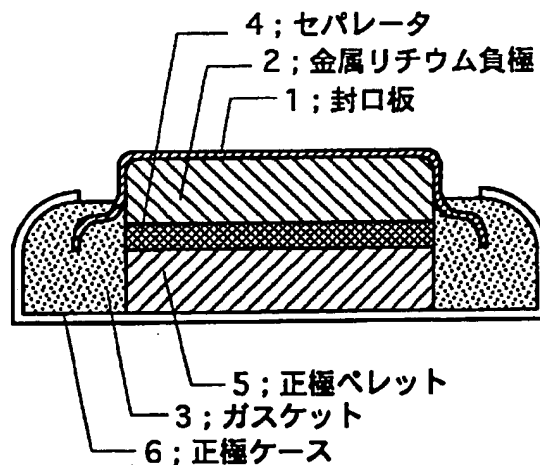
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(54) 【発明の名称】 リチウム二次電池

(57) 【要約】

【課題】 安価で4V以下の電圧で充放電が可能なリン酸鉄リチウム系材料を正極に用いたリチウム二次電池の、実用的な電流での放電容量を高める。 $z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$) で与えられるオリビン構造のリン酸化合物で、元素Xは該リン酸化合物を構成している状態では、リチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な物質であり、なおかつyが $0 < y \leq 0.3$ である物質を正極活物質5として使用した。

【効果】 無置換のリン酸鉄リチウムに比べて電解液の分解による電池寿命の低下が起りにくい4V以下の充放電において放電容量やサイクル特性を向上させることができた。



【特許請求の範囲】

【請求項1】 一般式 $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$) で与えられるオリビン構造のリン酸化合物で、元素Xは該リン酸化合物を構成している状態では、リチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な物質であり、なおかつyが $0 < y \leq 0.3$ である物質を正極活物質として含み、リチウム金属、リチウム合金またはリチウムイオンを吸蔵、放出可能な物質を負極活物質として、さらにリチウムイオンが前記正極活物質や前記負極活物質と電気化学反応をするための移動を行いうる物質を電解質として含むことを特徴とするリチウム二次電池。

【請求項2】 前記リン酸化合物中の元素Xがマグネシウム、コバルト、ニッケル、亜鉛の少なくとも1種類であることを特徴とする請求項1記載のリチウム二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明はリチウム二次電池に関し、特に正極活物質の改良に関わり、電池の放電容量の増加と充放電サイクル特性の向上を目指すものである。

【0002】

【従来の技術】 リチウム金属、リチウム合金あるいはリチウムイオンを吸蔵、放出可能な物質を負極活物質とするリチウム二次電池は、高い電圧と優れた可逆性を特徴としている。特に正極活物質としてリチウムと遷移金属との複合酸化物を用い、負極活物質として炭素系材料を用いたリチウムイオン二次電池は、従来の鉛二次電池やニッケル-カドミウム二次電池などに比べ軽量で容量も大きい。携帯電話やノート型パーソナルコンピュータなどの電子機器に広く用いられている。

【0003】 現在一般に用いられているリチウムイオン二次電池の正極活物質としては主に LiCoO_2 が用いられているが、 LiCoO_2 の原料であるコバルトは埋蔵量が少なく、しかも限られた地域でしか産出しないため、価格の面からも原料の安定供給の面からもリチウムイオン二次電池の正極活物質として好ましくない。

【0004】 これに対して産出量が多く安価な鉄を原料に用いた LiFePO_4 がリチウム二次電池の正極材料として動作することが特開平9-134725号などにより明らかにされている。また LiFePO_4 の鉄をコバルトで置換し電池電圧を制御することが特開平9-134724号に示されている。

【0005】

【発明が解決しようとする課題】 しかし、 LiFePO_4 は電池充放電時のリチウムの挿入脱離反応が遅く、電池内への正極活物質の充填密度を高めるために LiFePO_4 粒子のサイズを大きくすると、ごく小さな電流でしか満足な容量での充放電ができないという問題がある。

【0006】 また、 LiFePO_4 にコバルトを添加した場合、コバルトの酸化還元反応はリチウム金属の標準電位に対して5V程度の高い電位で起るが、充電電圧が4.3Vを越えると現在のリチウムイオン二次電池に使用されている電解液では電解液自身の酸化分解が起り、このような高い電圧での充放電はサイクル特性を劣化させる恐れが強い。高い電圧でも安定な電解液の開発が進められているものの、現在のところ実用化されているものはなく、必要以上にコバルトを添加することはコストの点からも電池の寿命の点からも好ましくない。

【0007】 従って、本発明は、前述した従来の課題を解決するためになされたものであり、その目的は、安価で4V以下の電圧で充放電が可能なリン酸鉄リチウム系材料を正極に用いたリチウム二次電池の、実用的な電流での放電容量を高めることにある。

【0008】

【課題を解決するための手段】 この様な目的を達成するために本発明によるリチウム二次電池は、一般式 $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$) で与えられるオリビン構造のリン酸化合物で、元素Xは該リン酸化合物を構成している状態では、リチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な物質であり、なおかつyが $0 < y \leq 0.3$ である物質を正極活物質として含み、リチウム金属、リチウム合金またはリチウムイオンを吸蔵、放出可能な物質を負極活物質として、さらにリチウムイオンが前記正極活物質や前記負極活物質と電気化学反応をするための移動を行いうる物質を電解質として含むことを特徴とするものである。

【0009】 また、本発明によるリチウム二次電池は、前述の発明において前記リン酸化合物中の元素Xがマグネシウム、コバルト、ニッケル、亜鉛の少なくとも1種類であることを特徴とするものである。

【0010】 本発明をさらに詳しく説明すると、本発明によるリチウム二次電池の正極活物質は、一般式 $\text{Li}_z\text{Fe}_{1-y}\text{X}_y\text{PO}_4$ ($0 < z \leq 1$) で与えられるオリビン構造のリン酸化合物で、元素Xは該リン酸化合物を構成している状態では、リチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な物質であり、なおかつyが $0 < y \leq 0.3$ である物質である。

【0011】 上述の様な一般的にリン酸鉄リチウムと呼ばれている物質は LiFePO_4 ($z=1$) で表され、構造を保ったままではリチウムをこれ以上挿入することはできない。この材料を電池の正極として用いた場合、充電を行うとリチウムが正極から抜けて行き、組成は FePO_4 に近づき (zが小さくなる)、充電した電池を放電すると、電解液中のリチウムが正極中に挿入され、組成が LiFePO_4 ($z=1$) に戻っていく。電池の放電容量や作製を考えると $z=1$ の材料が最も好ましいが、この様にzの値は連続的に変化するため、不定比な組成である $z=0.9$ などの組成の物質でも、一般的な

定比の組成である $z=1$ のリン酸鉄リチウムと同等の機構で動作する電池が作成可能である。このため、上記式中、 z は $0 < z \leq 1$ で示される。

【0012】 LiFePO_4 を正極材料に用いたリチウム二次電池においては、その充電の際にリチウムが脱離するとともに鉄イオンが2価から3価に変化する。リチウムが脱離した結果、その部分の結晶構造(オリビン構造)が不安定になり部分的にリチウムの移動経路が塞がれてしまい、更に内部にあるリチウムが脱離しにくくなることが、 LiFePO_4 を正極材料に用いたリチウム二次電池において実用的な充放電電流では十分な容量が得られない原因と考えられる。

【0013】また、この構造の不安定さが充放電サイクルを繰り返すことによる放電容量の減少を引き起こすことが考えられる。これに対して、リン酸化合物を構成している状態でリチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な亜鉛等の元素で一部の鉄を置き換えると、充電を行っても亜鉛等の置換した元素は2価のまま酸化されず、置換した元素に隣接するリチウムも脱離せずに結晶内に残る。このため、充電を行っても置換を行った部分は結晶構造が変化しにくく、リチウムの移動経路が確保されるために容量が増大すると共にサイクル安定性を向上させるものと考えられる。

【0014】しかし、脱離しないリチウムは充放電に関与しないため、この様な置換をあまり多く行くと電池の容量が減少してしまう。発明者は種々の実験を行い、容量増加の効果がみられる鉄元素の置換量が30% ($0 < y \leq 0.3$) 以下、好ましくは10%~30% ($0.1 \leq y \leq 0.3$)、さらに好ましくは10~20% ($0.1 \leq y \leq 0.2$) である事を見いだした。

【0015】なお、ここで述べたリチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な元素とは、まずアルカリ金属やアルカリ土類金属などのように、リチウム金属の標準電位に対して3V未満の電位で酸化還元が起り、それ以上高い電圧では安定な元素や、あるいはコバルトやニッケルなどのようにリン酸鉄リチウムの鉄と置換された状態では、リチウム金属の標準電位に対して3V未満の電位で2価から金属に還元され、3Vから4Vの電位領域では酸化還元が起らず、4Vを越える電位で2価から3価に酸化されるような元素をさす。

【0016】従って、置換する金属は遷移金属に限定されるものではなく、典型金属であってもかまわない。リン酸鉄リチウムのオリビン構造を維持したまま鉄と置換するためには、3Vから4Vの電位領域で2価のイオンであることが望ましく、置換する元素としてはマグネシウム、コバルト、ニッケル、亜鉛などが特に好ましい。

【0017】

【実施例】以下に図面を参照して本発明の実施例をより

詳細に説明する。なお、本発明は以下の実施例のみに限定されるものではない。

【0018】

【実施例1】図1は本発明によるリチウム二次電池の一実施例による構成を示した電池断面図である。図中、1は封口板、2は金属リチウム負極、3はガスケット、4はセパレータ、5は正極ペレット、6は正極ケースを示す。

【0019】図1の正極ペレット5に含まれる正極活物質である $\text{LiFe}_{0.7}\text{Co}_{0.3}\text{PO}_4$ は下記の方法で作製した。

【0020】まず原料である炭酸リチウム(Li_2CO_3)とシュウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)と酢酸コバルト4水和物($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で0.5:0.7:0.3:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。得られた物質のX線回折チャートを図2に示す。

【0021】報告されている LiFePO_4 のX線回折チャート(JCPDS 15-0760)とほぼ一致しており、オリビン構造を維持したまま鉄がコバルトによって置換されていることが分かる。この正極活物質70重量%と導電剤であるアセチレンブラック25重量%及び結着剤であるポリテトラフルオロエチレン5重量%を混練し、粘土状の塊としたものを2軸ローラーで厚さ0.6mm程度に圧延してからボンチで直径15mmの円板状に打ち抜いて正極ペレット5を作製した。図3に LiFePO_4 のオリビン構造を示す。黒丸がリチウム原子を、八面体は6個の酸素で囲まれた鉄を、四面体は4個の酸素で囲まれたリンをそれぞれ示している。

【0022】次にステンレス製の封口板1上に金属リチウムの負極2を加圧配置したものをポリプロピレン製ガスケット3の凹部に挿入し、負極の上にポリプロピレン製で微孔性のセパレータ4、正極ペレット5をこの順序に配置し、電解液として、エチレンカーボネートとジメチルカーボネートの等積混合溶媒に LiPF_6 を1mol/dm³濃度に溶解した電解液を適量注入して含浸させた後に、ステンレス製の正極ケース6を被せてかしめることにより、厚さ2mm、直径23mmのコイン型電池を作製した。作製した電池の充放電特性を充電終止電圧4.0V、放電終止電圧3.0V、1mA定電流という条件で充放電を行って評価した。

【0023】図4に10サイクル目の充放電曲線を示す。放電電位は、既に知られている置換を行っていないリン酸鉄リチウムを正極に、リチウム金属を負極に用いた電池の電圧とほぼ同一であり、鉄イオンの酸化還元により充放電が行われていることが分かる。放電容量は1サイクル目から10サイクル目にかけていくらか増加しその後はほぼ一定の容量を示した。

【0024】また、50サイクル目の容量は5.6mAhであった。初期50サイクルのサイクル回数と放電容量の関係を図5に示す。また元素Xによる鉄の置換量 y と50サイクル目の放電容量の関係を図6に示す。さらに電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1に示す。

【0025】

【比較例1】元素Xを含まない正極活物質である LiFePO_4 を下記の方法で作製した。まず原料である炭酸リチウム(Li_2CO_3)とシュウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で0.5:1:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。

【0026】得られた正極活物質を用いて実施例1と同

一の方法により正極ペレット及びコイン型電池を作製した。実施例1と同一の条件で充放電特性を評価したところ、1サイクル目の放電容量は実施例1に示した電池より高かったものの、5サイクル目から放電容量が実施例1に示した電池に比べて低くなり、50サイクル目では実施例1に示した電池の84%に相当する4.7mAhの容量しか得られなかった。

【0027】初期50サイクルのサイクル回数と放電容量の関係を図5に、また元素Xによる鉄の置換量 y と50サイクル目の放電容量の関係を図6に、さらに電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1に、それぞれ実施例1の値と併せて示す。

【0028】

【表1】実施例及び比較例に示した電池の正極活物質組成式、置換量 y と50サイクル目の放電容量

実施例及び比較例	組成式	置換量 y	50サイクル放電 容量 (mAh)
実施例1	$\text{LiFe}_{0.7}\text{Co}_{0.3}\text{PO}_4$	0.3	5.6
実施例2	$\text{LiFe}_{0.8}\text{Co}_{0.2}\text{PO}_4$	0.2	6.7
実施例3	$\text{LiFe}_{0.9}\text{Co}_{0.1}\text{PO}_4$	0.1	4.9
実施例4	$\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$	0.2	7.0
実施例5	$\text{LiFe}_{0.85}\text{Mg}_{0.15}\text{PO}_4$	0.15	6.8
実施例6	$\text{LiFe}_{0.8}\text{Ni}_{0.2}\text{PO}_4$	0.2	6.5
比較例1	LiFePO_4	0	4.7
比較例2	$\text{LiFe}_{0.6}\text{Co}_{0.4}\text{PO}_4$	0.4	4.3

【0029】

【実施例2】正極ペレットに含まれる正極活物質である $\text{LiFe}_{0.8}\text{Co}_{0.2}\text{PO}_4$ を下記の方法で作製した。まず原料である炭酸リチウム(Li_2CO_3)とシュウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)と酢酸コバルト4水和物($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で0.5:0.8:0.2:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。

【0030】得られた正極活物質を用いて実施例1と同一の方法により正極ペレット及びコイン型電池を作製した。実施例1と同一の条件で充放電特性を評価したところ放電容量が2サイクル目から比較例1に示した電池に比べて高くなり、50サイクル目では比較例1に示した電池の1.43倍にあたる6.7mAhの容量が得られた。

【0031】初期50サイクルのサイクル回数と放電容

量の関係を図5に、また元素Xによる鉄の置換量 y と50サイクル目の放電容量の関係を図6に、さらに電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1に、それぞれ実施例1及び比較例1の特性と併せて示す。

【0032】

【実施例3】正極ペレットに含まれる正極活物質である $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{PO}_4$ を下記の方法で作製した。まず原料である炭酸リチウム(Li_2CO_3)とシュウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)と酢酸コバルト4水和物($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で0.5:0.9:0.1:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。

【0033】得られた正極活物質を用いて実施例1と同一の方法によりコイン型電池を作製した。実施例1と同一の条件で充放電特性を評価したところ放電容量が5サ

イクル目から比較例1に示した電池に比べて高くなり、50サイクル目では比較例1に示した電池の1.04倍に相当する4.9mAhの容量が得られた。

【0034】初期50サイクルのサイクル回数と放電容量の関係を図5に、また元素Xによる鉄の置換量 y と50サイクル目の放電容量の関係を図6に、さらに電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1にそれぞれ実施例1、2及び比較例1の特性と併せて示す。

【0035】

【比較例2】正極ペレットに含まれる正極活物質である $\text{LiFe}_{0.6}\text{Co}_{0.4}\text{PO}_4$ を下記の方法で作製した。まず原料である炭酸リチウム(Li_2CO_3)とシュウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)と酢酸コバルト4水和物($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で0.5:0.6:0.4:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。

【0036】得られた正極活物質を用いて実施例1と同一の方法によりコイン型電池を作製した。実施例1と同一の条件で充放電特性を評価したところ放電容量が1サイクル目から50サイクル目まで常に比較例1に示した電池に比べて低くなり、50サイクル目では比較例1に示した電池の0.91倍に当たる4.3mAhの容量しか示さなかった。

【0037】初期50サイクルのサイクル回数と放電容量の関係を図5に、また元素Xによる鉄の置換量 y と50サイクル目の放電容量の関係を図6に、さらに電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1に、それぞれ実施例1から3及び比較例1の特性と併せて示す。

【0038】

【実施例4】正極ペレットに含まれる正極活物質である $\text{LiFe}_{0.8}\text{Zn}_{0.2}\text{PO}_4$ を下記の方法で作製した。まず原料である水酸化リチウム1水和物($\text{LiOH} \cdot \text{H}_2\text{O}$)とシュウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)と酢酸亜鉛2水和物($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で1:0.8:0.2:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。

【0039】得られた正極活物質を用いて実施例1と同一の方法によりコイン型電池を作製した。実施例1と同一の条件で充放電特性を評価したところ放電容量は1サイクル目から比較例1に示した電池に比べて高くなり、実施例2をやや上回るサイクル回数依存性を示した。また、50サイクル目では比較例1に示した電池の1.49倍に相当する7.0mAhの容量が得られた。

【0040】初期50サイクルのサイクル回数と放電容

量の関係を図5に、また、電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1に、それぞれ実施例1から3及び比較例1、2の特性と併せて示す。

【0041】

【実施例5】正極ペレットに含まれる正極活物質である $\text{LiFe}_{0.85}\text{Mg}_{0.15}\text{PO}_4$ を下記の方法で作製した。まず原料である水酸化リチウム1水和物($\text{LiOH} \cdot \text{H}_2\text{O}$)とシュウ酸鉄2水和物($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)と酸化マグネシウム(MgO)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で1:0.85:0.15:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。

【0042】得られた正極活物質を用いて実施例1と同一の方法によりコイン型電池を作製した。実施例1と同一の条件で充放電特性を評価したところ放電容量は1サイクル目から比較例1に示した電池に比べて高くなり、実施例2とほぼ同様なサイクル回数依存性を示した。

【0043】50サイクル目では比較例1に示した電池の1.45倍に当たる6.8mAhの容量が得られた。実施例5に示した電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1に、実施例1から4及び比較例1、2の特性と併せて示す。

【0044】

【実施例6】正極ペレットに含まれる正極活物質である $\text{LiFe}_{0.8}\text{Ni}_{0.2}\text{PO}_4$ を下記の方法で作製した。まず原料である水酸化リチウム1水和物($\text{LiOH} \cdot \text{H}_2\text{O}$)と酢酸鉄($(\text{CH}_3\text{COO})_2\text{Fe}$)と酸化ニッケル(NiO)とリン酸水素二アンモニウム($(\text{NH}_4)_2\text{HPO}_4$)をモル比で1:0.8:0.2:1となるように混合して坩堝に入れ、アルゴン雰囲気下で800℃で24時間焼成することにより作製した。

【0045】得られた正極活物質を用いて実施例1と同一の方法によりコイン型電池を作製した。実施例1と同一の条件で充放電特性を評価したところ放電容量は1サイクル目から比較例1に示した電池に比べて高くなり、実施例2をやや下回るサイクル回数依存性を示した。また、50サイクル目では比較例1に示した電池の1.38倍に相当する6.5mAhの容量が得られた。実施例6に示した電池の正極活物質組成式、置換量 y と50サイクル目の放電容量を表1に、実施例1から5及び比較例1、2の特性と併せて示す。

【0046】なお、前述した実施例において、正極としてはペレット状に整形したものをを用いたが、N-メチル-2-ピロリドンの様な溶媒に正極活物質とポリフッ化ビニリデンの様なバインダを加えてスラリーを作製し、それを金属箔上に薄く塗布乾燥した塗布電極の様な形状でも構わない。

【0047】また、負極材料としてはリチウム金属を用いたが、他にリチウム合金、黒鉛やコークスなどの炭素

系材料、タングステン酸化物、ニオブ酸化物、バナジウム酸化物、スズ酸化物などの金属酸化物、リチウムマンガニウム酸化物やリチウムコバルト酸化物、リチウム鉄酸化物などのリチウム遷移金属複合酸化物、硫化鉄や硫化モリブデン等の金属カルコゲナイトなどでも構わない。

【0048】さらに電解液としてはエチレンカーボネートとジメチルカーボネートの等積混合溶媒に LiPF_6 を $1\text{mol}/\text{dm}^3$ 濃度に溶解した電解液を用いたが、従来の非水系リチウム二次電池と同様なものも使用可能である。

【0049】例えば溶媒としてはジメトキシエタン、2-メチルテトラヒドロフラン、エチレンカーボネート、メチルホルメート、ジメチルスルホキシド、プロピレンカーボネート、アセトニトリル、ジメチルカーボネート、ジエチルカーボネート、メチルエチルカーボネートなどを単独で、あるいは2種類以上を混合して使用することが可能である。

【0050】また、溶質としては実施例において用いた LiPF_6 以外にも、例えば、 LiClO_4 、 LiBF_4 、 LiAsF_6 、 LiCF_3SO_3 等でも構わない。更に、ポリマー電解質、固体電解質、常温溶融塩等も使用可能である。また、セパレータや電池ケース等の構造材料等の他の要素についても従来公知の各種材料が使用可能である。さらに電池形状についても実施例においてはボタン型としたが、特に制限されるものではなく、円筒型、角型等の形状でもかまわない。

【0051】

【発明の効果】以上説明したように、本発明によるリチウム二次電池によれば、正極活物質として、リン酸鉄リチウム中の鉄を、リン酸化合物を構成している状態では

リチウム金属の標準電位に対して3Vから4Vの電位領域で電気化学的に安定な物質により30%以下の割合で置き換えた化合物を用いることにより、無置換のリン酸鉄リチウムに比べて電解液の分解による電池寿命の低下が起りにくい4V以下での充放電において放電容量やサイクル特性を向上させることができた。従って経済的に優れてなおかつ電池特性の良好なリチウム二次電池の実現が可能となった。

【図面の簡単な説明】

【図1】本発明によるリチウム二次電池の一実施例による構成を示した断面図。

【図2】本発明のリチウム二次電池の実施例1において正極活物質として用いた $\text{LiFe}_{0.7}\text{Co}_{0.3}\text{PO}_4$ のX線回折パターンを示した図。

【図3】 LiFePO_4 のオリビン構造を示す図。

【図4】本発明のリチウム二次電池の実施例1における電池の充放電曲線を示した図。

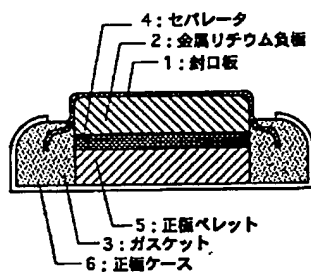
【図5】本発明のリチウム二次電池の実施例1～4におけるサイクル回数と放電容量の関係を比較例1、2における関係と併せて示した図。

【図6】本発明のリチウム二次電池の実施例1～3における元素Xによる鉄の置換量yと放電容量の関係を比較例1、2における関係と併せて示した図。

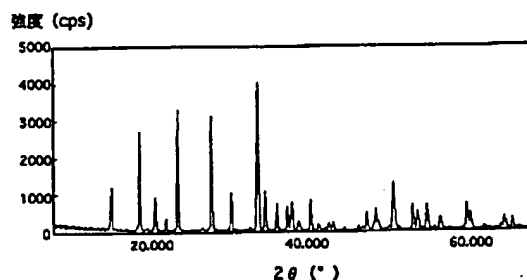
【符号の説明】

- | | |
|---|----------|
| 1 | 封口板 |
| 2 | 金属リチウム負極 |
| 3 | ガスケット |
| 4 | セパレータ |
| 5 | 正極ベレット |
| 6 | 正極ケース |

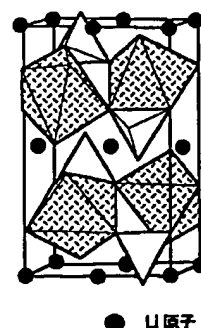
【図1】



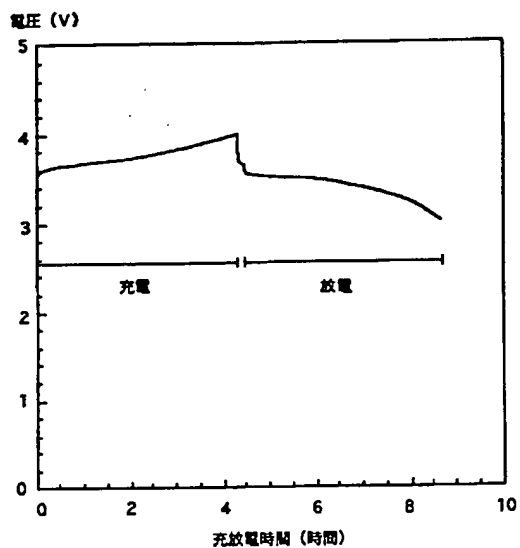
【図2】



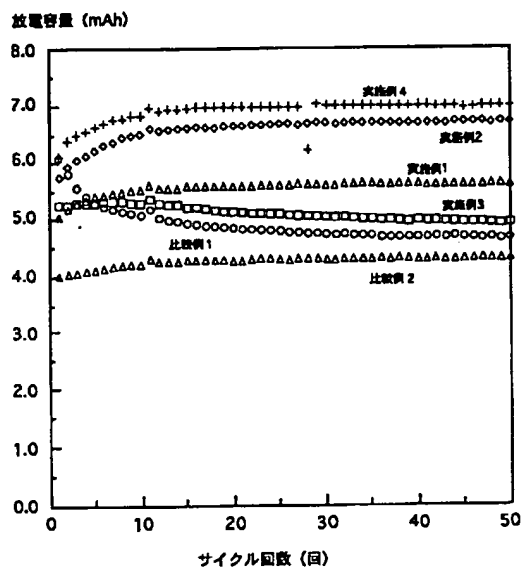
【図3】



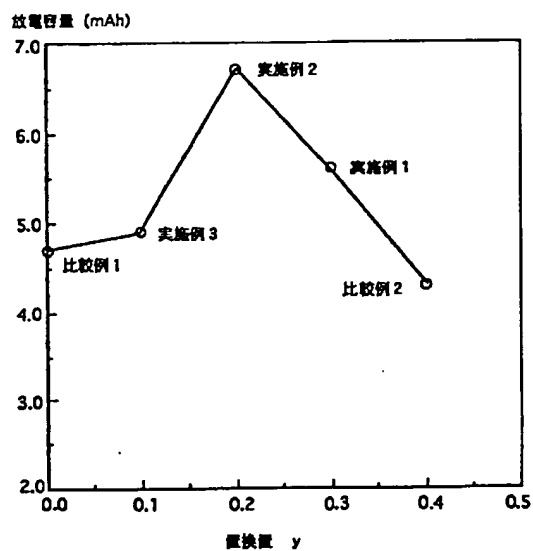
【図4】



【図5】



【図6】



フロントページの続き

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